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Title: US-DOE and Republic of South Africa Uranium Benchmarking Study Report: Results From Los Alamos National Laboratory

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INTRODUCTION

This report details work performed at Los Alamos National Laboratory (LANL) in support of an interlaboratory uranium (U) benchmarking collaboration between LANL, Lawrence Livermore National Laboratory (LLNL), and South African Nuclear Energy Corporation (Necsa). The goal of this interlaboratory benchmarking exercise is to compare analytical methods and data obtained on uranium reference materials CUP-2 and New Brunswick Laboratory (NBL) certified reference material (CRM) 124-2. The LANL commitments for this project include performing microwave digestion of fresh CUP-2 and CRM 124-2 powders, measuring the U isotope composition of CUP-2 and CRM 124-2 by both single-collector and multi-collector inductively coupled plasma mass spectrometry (SC-ICP-MS and MC-ICP-MS, respectively), and determining trace-element abundances in CUP-2 and CRM 124-2 by inductively coupled plasma mass spectrometry (ICP-MS). This report details the methods employed by LANL in support of these objectives and presents the data obtained during this collaborative exercise.

SAMPLE DESCRIPTION

The samples analyzed during this collaborative exercise consist of uranium ore concentrate (UOC) reference material CUP-2 and uranium oxide reference material CRM 124-2.

Reference material CUP-2 was produced in 1986 as a joint effort between the Canadian Certified Reference Materials Project (CCRMP) and the Analytical Subcommittee of the Canadian Uranium Producers Metallurgical Committee. The material was subsequently checked for homogeneity and distributed in 25 g units to 17 laboratories for characterization of uranium content, moisture, and 15 additional analytes. The CUP-2 Certificate of Analysis was issued in June 1988.

Certified reference material 124-2 is a uranium oxide (U_3O_8) impurity reference material distributed by the U.S. Department of Energy New Brunswick Laboratory as part of the 124 series consisting of reference materials 124-1 through 124-7. Certified reference material 124-2 is doped with 24 impurity elements, which were added in solution and blended with the uranium oxide matrix material. Initial impurity certificate reference values were provided in 1983 for the 124 series, and the series was reevaluated in 2009 (Bürger *et al.* 2009). Certified impurity values for the 124 series are based on the gravimetric preparation of the reference materials, and the uncertainties are based on the reevaluation of the series performed by Bürger *et al.* in 2009.

SAMPLE PREPARATION

To prepare CUP-2 for trace element determination, twelve nominally 0.1 g aliquots of CUP-2 powder were weighed and digested in 20 mL 8 M HNO_3 and 0.1 mL concentrated HF in closed vials on a hotplate at 90 °C for 48 hours. Dissolutions were performed in pre-cleaned Savillex PFA vials. Following the hotplate digestion, the CUP-2 solutions were quantitatively transferred from the vials into pre-cleaned and weighed 125 mL Teflon bottles.

Powders of CUP-2 and CRM 124-2 were digested in a microwave prior to U isotope composition analysis as follows. Approximately 0.5 g of CUP-2 and 1 g of CRM 124-2 powders were transferred into pre-cleaned quartz crucibles and dried overnight in a muffle furnace at 100 °C. The dried powders were transferred to tared weigh papers and then transferred to pre-cleaned Teflon microwave digestion vessels. The weigh papers were weighed following the transfer of the powders to determine the weight delivered to the microwave vessels for digestion. Prior to adding the sample powder, the microwave vessels were filled with 1 mL of 18.2 MΩ cm water to minimize possible sample loss due to static. Following the addition of the sample powder, a solution containing 14 mL of concentrated HNO_3 plus 0.09 M HF was added to the vessels. The samples were digested in a Milestone Ethos HP microwave by using a 20-minute ramp to 180 °C, a 30-minute hold at 180 °C, and a ramp down to ambient room temperature. Process blanks were included with the CUP-2 and CRM 124-2 powders using the same digestion reagents and microwave procedure. Following digestion, the sample solutions were transferred from the microwave digestion vessels into pre-cleaned and weighed 125 mL Teflon bottles. The microwave vessels were rinsed twice with concentrated HNO_3 to ensure quantitative sample transfer, and the rinsate was added to the sample bottles. The primary sample solutions were diluted to 100 mL 4 M HNO_3 with trace HF solutions, and the bottles were weighed to determine the weight of the primary sample solutions. The primary solution of CRM 124-2 created following these methods was also used for trace element determination.

Serial dilutions of the primary solutions were prepared by weighing aliquots of the primary sample solutions into pre-cleaned 125 mL Teflon bottles, diluting to a total volume of

approximately 100 mL with 4 M HNO_3, and weighing the bottles again. Primary solutions of CUP-2 and the associated process blank were diluted twice to yield a working tertiary dilution for U isotope composition aliquots. The tertiary dilution of CUP-2 contains approximately 21.5 ng of U per gram of solution. Primary solutions of CRM 124-2 and the associated process blank were diluted three times to yield a working quaternary dilution for U isotope composition aliquots. The quaternary dilution of CRM 124-2 contains approximately 7.9 ng of U per gram of solution.

TRACE ELEMENT COMPOSITION

Overview

Elemental impurities present in trace quantities in uranium materials (e.g., uranium metals, oxides, or ore concentrates) may provide information about the provenance or processing of the uranium material. Therefore, the accurate and precise determination of trace element abundances in uranium reference materials is an important capability for nuclear forensics laboratories to develop and test. As part of this collaborative interlaboratory benchmarking exercise, LANL analyzed trace element abundances in CUP-2 and CRM 124-2 by single-collector ICP-MS. The trace element data obtained by LANL are for comparison to the trace element data obtained by LLNL (using both quadrupole ICP-MS and single-collector ICP-MS) and by Necsa (using quadrupole ICP-MS).

Trace Element Aliquots and Sample Preparation

A secondary dilution of each of the twelve CUP-2 primary solutions was prepared gravimetrically to have a nominal U concentration of 100 micrograms per gram (µg U/g or ppm U). The secondary dilution was used to prepare sample aliquots for trace element analysis. To produce a CRM 124-2 solution for trace element analysis, approximately 1.5 g of the CRM 124-2 primary solution was weighed into a pre-cleaned and weighed Teflon bottle. Approximately 100 mL of 2% HNO_3 was added, resulting in a working solution containing a U concentration of approximately 100 µg U/g. The CRM 124-2 trace element solution was measured in triplicate. All trace element solutions were prepared within 48 hours of primary solution preparation to avoid precipitation effects, and trace element measurements were run by ICP-MS within one week of sample preparation.

Trace Element Inductively Coupled Plasma Mass Spectrometry Measurements

Trace element dilutions of each dissolved sample were mixed with an indium (In) internal standard solution prior to analysis to yield an In concentration of 5 ppb and a nominal U concentration of 100 ppm in each trace element analysis tube. Trace element measurements were run against three sets of matrix-matched external calibration standards. Separate sets of external calibration standards were used to make interference corrections (primarily oxide interferences on lanthanide elements) and to maximize calibration standard solution stability. Calibration standards were purchased as custom prepared standards from Inorganic Ventures™ and were gravimetrically prepared to match the matrix of the samples with U concentrations of 100 µg U/g. The calibration standards were prepared within 48 hours of sample analysis to ensure the trace elements of interest remained in solution. Natural U metal certified reference material, NBS

SRM 960, was dissolved in ultra-pure reagents to use as a source of U for matrix matching purposes. Two 100 µg U/g solutions of SRM 960 were prepared and measured as matrix blanks during each analysis session. Trace element measurements were made using a Thermo Element XR ICP-MS. The ICP-MS was tuned prior to each analysis session to obtain a minimum count rate of 2.0×10^6 counts per second (cps) per ng/g $^{115}In^+$ and $^{238}U^+$, 150,000 cps $^{7}Li^+$ and a $UO^+/^{238}U^+$ less than 10%. Prior to each analysis session, the analog correction (ACF) and Faraday correction (FCF) factors were adjusted in the software registry settings until detector responses in complementary modes were identical. A solution containing moderate concentrations of each analyte measured was used to update trace element mass offsets prior to each analysis session. Analyte isotopes of interest were measured in one or more preset mass resolution modes of low (M/ΔM = 400), medium (M/ΔM=4,000) and high resolution (M/ΔM =10,000).

Trace Element Critical Levels and Uncertainty

Critical levels (L_c) for trace elements are reported in **Tables 1** and **4**. The critical level is based on the method outlined by Currie (1968) and represents a value above which a signal can be detected but not necessarily quantified. To calculate critical levels for both CRM 124-2 and CUP-2, the standard deviations on intensities measured in seven process blanks was multiplied by 2.33, then divided by the sensitivity for that analyte. The critical levels reported in **Tables 1** and **4** account mathematically for the manner in which the analysis solution was diluted assuming the measurement was made in a solution containing 100 µg U/g analysis solution. The units for the L_C values reported in **Tables 1** and **4** below are in units of µg analyte/g sample. If a trace element was analyzed but not detected above the critical level, it is reported in **Tables 1** and **4** as < x, where x represents the L_c.

The uncertainties reported for individual trace element measurements in **Tables 1** through **3** are reported as combined uncertainties at the 95% confidence level (k=2). Average trace element measurements are also reported in **Tables 1** and **4**. Given the small population used to calculate the reported average trace element compositions (n=3 for CRM 124-2 and n=12 for CUP-2), the 95% (2-sigma) external uncertainties provided for the average of the measurements in **Tables 1** and **4** were calculated using the following equation:

$$u = \bar{X} \pm t_{\left(1-\frac{\alpha}{2}\right),v}(\sigma/\sqrt{N_r})$$

Where $t_{(1-\alpha/2)}$ is the $100(1-\alpha/2)^{th}$ percentile of the t-distribution corresponding to a probability $\alpha = 0.05$, N_r = number of replicates, and $v = N_r - 1$ degrees of freedom. This calculation provides the uncertainty of the mean of the replicate trace element measurements at the 95% confidence level.

Results

Trace element concentrations obtained for CRM 124-2 and CUP-2 are presented in **Tables 1** through **3** below. Trace element concentrations are reported in units of micrograms of trace element per gram of sample.

A total of 48 trace elements were analyzed in CRM 124-2; of these, 20 were detected at a concentration above the critical level for that element. The 20 trace elements detected above the

critical level in CRM 124-2 are elements that were added as impurities during the preparation of CRM 124-2. Four additional elemental impurities (B, Si, Ag, and Ti) are present in CRM 124-2; however, these elements were not targeted for analysis in this study. The average trace element concentrations obtained for CRM 124-2 are compared to the reference values in **Table 1**. In general, the trace element concentrations obtained show good agreement with the certified reference values. With the exception of Zr, all average measured trace element values agree with the CRM 124-2 certified values within uncertainty. The averaged LANL measured Zr concentration in CRM 124-2 of 124.9 ± 1.1 μg Zr /g sample was higher than the CRM 124-2 certified value of 85 ± 27 μg Zr /g sample. Additionally, the reproducibility of the trace element measurements for most elements was generally good: the average relative uncertainty on the mean CRM 124-2 values reported here is approximately 10%. Two exceptions are Al, which has a relative uncertainty on the mean value of 49%, and Mo, which was detected above the critical level in only two of the three analytical sessions and has a relative uncertainty on the mean value of 21%.

Results for CUP-2 analytical sessions A and B are reported in **Table 2**, results for analytical session C and D are reported in **Table 3**, and average results for all analytical sessions are reported in **Table 4** below. Forty-four trace elements were analyzed in CUP-2; of these, all but two (Be and Ru) were detected at a concentration above the respective critical level for that element.

The average trace element concentrations obtained for CUP-2 are compared to the reference values in **Table 4**. The trace element concentrations obtained for CUP-2 show variable agreement with the certified reference values (which it is worth noting do not have an associated uncertainty provided on the CUP-2 certificate). The average measured trace element abundance agreed with the certificate value for CUP-2 for only two elements, B and V. For the elements that did not agree with the certificate value, the bias from the certificate value ranged from −19% for Ni to +14% for Ca. The average bias for all elements that were measured and listed on the CUP-2 certificate is +1%. Trace element abundances in CUP-2 were initially measured in units of μg/g U and were converted to units of μg/g sample using the U content and associated uncertainty provided on the certificate. The U content listed on the CUP-2 certificate was measured on a dry basis, whereas the U content in the trace element solutions—which was used to report trace element abundances in units of μg/g U—was measured on an as-received basis. However, given the small average bias obtained between measured and certificate values, a correction for hydration in CUP-2 (listed as 2.94% on the certificate) was not performed. A hydration correction can be calculated and applied using the data in this report if needed.

The reproducibility of the trace element measurements for most elements in CUP-2 reported here was generally good: the average relative uncertainty on the mean CUP-2 values for all elements measured is approximately 4%, and the relative uncertainty on the mean for most element concentrations is better than 12%. The only exception is Ge, which has a relative uncertainty of approximately 26% for the mean value.

Table 1. Measured Trace Element Compositions for CRM 124-2.

CRM 124-2 Trace Element Data[a]													
Atomic Number	**Element**	**124-2 A**	***Unc. (k=2)***	**124-2 B**	***Unc. (k=2)***	**124-2 C**	***Unc. (k=2)***	**L_c Session 1[b]**	**L_c Session 2**	**124-2 Avg.**	***Unc. (k=2)[c]***	**Certified Value**	***Unc. (k=2)***
3	Li	< 0.073	--	< 0.059	--	< 0.059	--	0.073	0.059	--	--	--	--
4	Be	10.39	0.53	9.93	0.20	10.36	0.24	0.18	0.19	10.23	0.63	10.6	1.4
11	Na	158.2	9.0	169	14	162	15	14	5.8	163	14	170	36
12	Mg	42.0	2.1	45.3	1.7	39.2	3.9	2.1	2.6	42.2	7.6	43.2	8.5
13	Al	80.6	2.1	121.8	4.1	71.8	2.8	3.4	10	91	66	89	12
19	K	< 35	--	< 17	--	< 17	--	35	17	--	--	--	--
20	Ca	87.3	6.7	93	21	87.0	3.6	10	13	89.1	8.5	85	19
23	V	20.6	1.2	20.70	0.54	19.76	0.43	1.0	0.079	20.3	1.3	21.2	2.4
24	Cr	46.4	4.0	42.1	3.5	45.1	3.4	0.064	0.068	44.5	5.5	44.1	5.5
25	Mn	21.7	1.4	20.94	0.94	20.20	0.90	0.18	0.17	21.0	1.9	22.0	2.0
26	Fe	111.4	7.4	95.2	9.9	109.0	4.4	24	31	105	22	93	11
27	Co	10.03	0.40	10.19	0.59	10.08	0.27	0.013	0.0075	10.10	0.20	10.6	2.1
28	Ni	86.4	4.0	85.9	6.0	79.7	9.1	0.31	0.60	84.0	9.3	86.5	6.1
29	Cu	22.5	1.7	21.1	1.1	21.86	0.86	0.11	0.11	21.8	1.7	21.2	4.4
30	Zn	105.9	6.6	96.6	6.4	105	11	0.41	0.53	103	13	86	11
31	Ga	< 0.0092	--	< 0.0049	--	< 0.0049	--	0.0092	0.0049	--	--	--	--
33	As	< 0.11	--	< 0.061	--	< 0.061	--	0.11	0.061	--	--	--	--
37	Rb	< 0.047	--	< 0.039	--	< 0.039	--	0.047	0.039	--	--	--	--
38	Sr	< 0.033	--	< 0.038	--	< 0.038	--	0.033	0.038	--	--	--	--
40	Zr	124.8	3.5	125.4	4.0	124.5	4.1	0.049	0.0021	124.9	1.1	85	27
41	Nb	< 0.0086	--	< 0.0060	--	< 0.0060	--	0.0086	0.0060	--	--	--	--
42	Mo	< 41	--	39.5	2.4	42.1	1.5	41	26	41	17	42.4	3.6
48	Cd	2.37	0.42	2.04	0.61	2.01	0.61	0.48	0.36	2.14	0.49	2.29	0.30
50	Sn	20.00	0.72	20.5	1.5	20.31	0.51	0.035	0.040	20.28	0.68	22.0	4.6
51	Sb	< 0.013	--	< 0.013	--	< 0.013	--	0.013	0.013	--	--	--	--
55	Cs	< 0.0024	--	< 0.0014	--	< 0.0014	--	0.0024	0.0014	--	--	--	--
56	Ba	< 0.81	--	< 0.91	--	< 0.91	--	0.81	0.91	--	--	--	--
57	La	< 0.0013	--	< 0.0016	--	< 0.0016	--	0.0013	0.0016	--	--	--	--
58	Ce	< 0.013	--	< 0.0027	--	< 0.0027	--	0.013	0.0027	--	--	--	--
59	Pr	< 0.069	--	< 0.073	--	< 0.073	--	0.069	0.073	--	--	--	--
60	Nd	< 0.33	--	< 0.36	--	< 0.36	--	0.33	0.36	--	--	--	--

CRM 124-2 Trace Element Data Continued[a]													
Atomic Number	**Element**	**124-2 A**	***Unc. (k=2)***	**124-2 B**	***Unc. (k=2)***	**124-2 C**	***Unc. (k=2)***	**L_c Session 1[b]**	**L_c Session 2**	**124-2 Avg.**	***Unc. (k=2)[c]***	**Certified Value**	***Unc. (k=2)***
62	Sm	< 0.88	--	< 1.0	--	< 1.0	--	0.88	1.0	--	--	--	--
63	Eu	< 0.0011	--	< 0.0016	--	< 0.0016	--	0.0011	0.0016	--	--	--	--
64	Gd	< 0.010	--	< 0.0066	--	< 0.0066	--	0.010	0.0066	--	--	--	--
65	Tb	< 0.00029	--	< 0.00018	--	< 0.00018	--	0.00029	0.00018	--	--	--	--
66	Dy	< 0.0030	--	< 0.0052	--	< 0.0052	--	0.0030	0.0052	--	--	--	--
67	Ho	< 0.00032	--	< 0.00018	--	< 0.00018	--	0.00032	0.00018	--	--	--	--
68	Er	< 0.0017	--	< 0.0011	--	< 0.0011	--	0.0017	0.0011	--	--	--	--
69	Tm	< 0.00024	--	< 0.00027	--	< 0.00027	--	0.00024	0.00027	--	--	--	--
70	Yb	< 0.0018	--	< 0.00090	--	< 0.00090	--	0.0018	0.00090	--	--	--	--
71	Lu	< 0.00044	--	< 0.00015	--	< 0.00015	--	0.00044	0.00015	--	--	--	--
72	Hf	< 0.00084	--	< 0.00079	--	< 0.00079	--	0.00084	0.00079	--	--	--	--
73	Ta	< 0.00032	--	< 0.00035	--	< 0.00035	--	0.00032	0.00035	--	--	--	--
74	W	75.1	2.8	92.3	5.6	88.5	5.6	2.7	0.70	85	23	85	10
81	Tl	< 0.00039	--	< 0.00047	--	< 0.00047	--	0.00039	0.00047	--	--	--	--
82	Pb	21.40	0.81	23.0	2.7	23.0	2.9	0.26	0.24	22.5	2.3	22.0	6.2
83	Bi	22.4	1.3	23.4	2.7	23.3	2.8	0.0061	0.0086	23.0	1.5	21.2	6.0
90	Th	< 0.0049	--	< 0.014	--	< 0.014	--	0.0049	0.014	--	--	--	--

[a] Trace element compositions were analyzed on January 28, 2020 (124-2 A, Session 1) and January 29, 2020 (124-2 B and 124-2 C, Session 2).
[b] L_C = Critical level, level above which an element is detected but not necessarily quantifiable.
[c] Uncertainty on the average measured CRM 124-2 value is calculated as described in the text.
[d] Certificate values for all trace elements were converted from units of µg/g U to units of µg/g sample using a factor of 0.848 g/g without additional uncertainty as recommended by the CRM 124-2 Certificate of Analysis.
[d] All trace element compositions are reported in units of µg/g sample.

Table 2. Trace Element Compositions for CUP-2 analytical sessions A and B.

Sessions A and B CUP-2 Trace Element Data[a]													
Atomic Number	**Element**	**CUP-2 A-1**	***Unc. (k=2)***	**CUP-2 A-2**	***Unc. (k=2)***	**CUP-2 A-3**	***Unc. (k=2)***	**CUP-2 B-1**	***Unc. (k=2)***	**CUP-2 B-2**	***Unc. (k=2)***	**CUP-2 B-3**	***Unc. (k=2)***
3	Li	0.861	0.019	0.932	0.016	0.914	0.025	0.947	0.022	0.936	0.030	0.976	0.036
4	Be	< 0.33	--	< 0.33	--	< 0.33	--	< 0.33	--	< 0.33	--	< 0.33	--
5	B	52.18	0.77	54.79	0.86	55.16	0.74	51.4	1.8	50.0	1.5	50.5	2.0
11	Na	4665	127	4712	130	4621	136	4702	129	4528	130	4593	130
12	Mg	2542	42	2508	40	2547	51	2349	44	2356	45	2279	46
13	Al	2435	62	2461	64	2445	66	2644	60	2568	50	2566	68
19	K	1333	25	1283	24	1272	24	1126	23	1135	29	1072	23
20	Ca	7444	89	7256	83	7274	90	6639	113	6820	122	6555	131
22	Ti	167.8	2.9	170.0	2.5	165.8	2.1	174.0	3.0	167.5	2.3	163.3	2.7
23	V	655	22	683	24	672	24	673	36	673	38	678	38
24	Cr	16.59	0.26	15.71	0.23	15.05	0.30	14.67	0.29	15.25	0.34	14.72	0.34
25	Mn	105.8	2.7	110.5	2.9	110.6	3.0	105.7	6.3	103.9	6.3	103.5	6.3
26	Fe	3307	46	3315	44	3245	53	3331	40	3271	38	3302	44
27	Co	2.031	0.023	2.087	0.027	2.062	0.025	2.319	0.046	2.194	0.033	2.237	0.034
28	Ni	22.34	0.54	23.33	0.61	21.98	0.50	23.82	0.67	23.21	0.56	24.70	0.62
29	Cu	24.03	0.58	24.01	0.55	25.36	0.58	23.89	0.57	23.51	0.58	22.82	0.59
30	Zn	32.46	0.84	32.54	0.85	31.95	0.99	31.2	1.4	30.2	1.1	29.72	0.92
31	Ga	0.322	0.014	0.323	0.019	0.310	0.010	0.329	0.020	0.341	0.027	0.327	0.019
32	Ge	0.042	0.022	0.054	0.024	0.076	0.020	0.063	0.033	0.053	0.022	0.042	0.049
33	As	384.3	5.7	376.7	4.5	343.8	5.5	387.6	6.1	379.9	6.2	392.0	4.5
37	Rb	7.88	0.11	7.87	0.13	7.63	0.13	7.61	0.16	7.476	0.091	7.39	0.14
38	Sr	50.87	0.71	52.16	0.76	52.38	0.64	52.22	0.83	51.16	0.81	50.82	0.73
40	Zr	399	11	415	11	406	10	396.4	7.8	384.9	7.8	391.1	8.9
41	Nb	0.601	0.020	0.404	0.012	0.383	0.012	0.386	0.017	0.382	0.018	0.387	0.015
42	Mo	699	14	729	13	720	14	709	13	701	13	712	13
44	Ru	< 0.018	--	< 0.018	--	< 0.018	--	< 0.018	--	< 0.018	--	< 0.018	--
45	Rh	0.01568	0.00048	0.01578	0.00086	0.01618	0.00069	0.01141	0.00069	0.0109	0.0012	0.01111	0.00075
48	Cd	2.834	0.060	2.847	0.044	2.861	0.085	3.163	0.075	2.906	0.056	2.90	0.11
50	Sn	3.183	0.088	3.313	0.077	3.140	0.073	3.47	0.11	3.430	0.091	3.455	0.090
51	Sb	0.1282	0.0080	0.126	0.015	0.111	0.021	0.1196	0.0029	0.1169	0.0017	0.1276	0.0040
55	Cs	0.946	0.011	0.983	0.013	0.970	0.012	0.995	0.013	0.963	0.015	0.967	0.014

Sessions A and B CUP-2 Trace Element Data Continued[a]													
Atomic Number	**Element**	**CUP-2 A-1**	***Unc. (k=2)***	**CUP-2 A-2**	***Unc. (k=2)***	**CUP-2 A-3**	***Unc. (k=2)***	**CUP-2 B-1**	***Unc. (k=2)***	**CUP-2 B-2**	***Unc. (k=2)***	**CUP-2 B-3**	***Unc. (k=2)***
56	Ba	114.8	1.7	112.9	1.9	112.6	2.0	106.5	2.1	102.8	2.1	102.4	2.0
57	La	19.06	0.27	18.84	0.25	18.23	0.24	19.86	0.30	19.32	0.31	19.31	0.34
58	Ce	35.6	1.3	36.6	1.3	35.9	1.3	42.08	0.62	40.59	0.61	40.34	0.64
59	Pr	4.32	0.11	4.34	0.11	4.32	0.11	4.960	0.067	4.785	0.080	4.745	0.080
60	Nd	19.24	0.34	19.04	0.51	18.34	0.35	21.13	0.36	20.18	0.32	19.91	0.35
62	Sm	9.36	0.17	9.25	0.19	8.97	0.20	10.06	0.22	9.79	0.16	9.64	0.19
63	Eu	0.754	0.011	0.761	0.020	0.729	0.021	0.844	0.029	0.805	0.022	0.821	0.014
64	Gd	15.05	0.22	14.88	0.26	14.52	0.21	16.64	0.24	15.95	0.31	15.98	0.50
65	Tb	2.844	0.039	2.842	0.040	2.775	0.032	3.085	0.047	2.951	0.090	2.944	0.046
66	Dy	17.70	0.29	17.67	0.31	17.19	0.26	19.34	0.32	18.38	0.26	18.05	0.31
67	Ho	3.132	0.038	3.116	0.047	3.036	0.041	3.460	0.062	3.293	0.051	3.275	0.049
68	Er	8.31	0.15	8.23	0.11	8.06	0.14	9.03	0.18	8.63	0.12	8.59	0.16
69	Tm	1.080	0.014	1.075	0.037	1.051	0.014	1.200	0.019	1.140	0.016	1.126	0.019
70	Yb	6.46	0.12	6.42	0.12	6.37	0.10	7.19	0.14	6.85	0.14	6.70	0.13
71	Lu	0.831	0.017	0.831	0.021	0.778	0.019	0.916	0.030	0.905	0.014	0.896	0.022
72	Hf	0.238	0.014	0.245	0.011	0.241	0.011	0.231	0.032	0.230	0.020	0.266	0.015
73	Ta	0.0262	0.0020	0.02544	0.00083	0.0271	0.0015	0.0282	0.0022	0.0317	0.0019	0.0331	0.0026
74	W	12.90	0.31	13.46	0.32	12.91	0.32	13.08	0.26	12.90	0.27	13.90	0.28
75	Re	0.02723	0.00093	0.02820	0.00074	0.0275	0.0013	0.0300	0.0013	0.0299	0.0013	0.0300	0.0017
77	Ir	0.00267	0.00013	0.00279	0.00028	0.00271	0.00041	0.00303	0.00063	0.002548	0.000076	0.00295	0.00037
78	Pt	0.00330	0.00026	0.00354	0.00077	0.00306	0.00060	0.00455	0.00040	0.0048	0.0015	0.0045	0.0013
81	Tl	3.192	0.054	3.278	0.056	3.243	0.063	3.304	0.063	3.230	0.058	3.196	0.061
82	Pb	263.0	9.1	269.6	9.5	260.1	9.3	271	14	269	15	268	14
83	Bi	1.155	0.014	1.206	0.012	1.167	0.016	1.246	0.013	1.207	0.018	1.240	0.013
90	Th	1496	20	1600	24	1563	22	1612	37	1551	39	1525	40

[a] Trace element compositions for CUP-2 solutions were analyzed in triplicate during four analytical sessions in 2017: January 27 (CUP-2 A), January 30 (CUP-2 B), January 31 (CUP-2 C), and February 1 (CUP-2 D).

[b] All trace element data are reported in units of µg/g sample. Trace elements were originally measured here in units of µg/g U, and were converted to units of µg/g sample using the U content provided on the CUP-2 certificate. Note that no correction for hydration differences between trace element contents measured here on an "as received" basis and U content measured for the certificate value on a dry basis has been made.

Table 3. Trace Element Compositions for CUP-2 analytical sessions C and D.

Sessions C and D CUP-2 Trace Element Data[a]													
Atomic Number	**Element**	**CUP-2 C-1**	***Unc. (k=2)***	**CUP-2 C-2**	***Unc. (k=2)***	**CUP-2 C-3**	***Unc. (k=2)***	**CUP-2 D-1**	***Unc. (k=2)***	**CUP-2 D-2**	***Unc. (k=2)***	**CUP-2 D-3**	***Unc. (k=2)***
3	Li	0.914	0.017	0.933	0.023	0.911	0.024	0.941	0.022	0.88	0.030	0.851	0.030
4	Be	< 0.33	--	< 0.33	--	< 0.33	--	< 0.33	--	< 0.33	--	< 0.33	--
5	B	53.89	0.83	53.91	0.83	51.11	0.87	51.1	1.8	50.1	1.6	48.9	1.7
11	Na	4711	136	4648	138	4633	140	5084	148	5168	153	5049	154
12	Mg	2534	47	2478	50	2462	42	2492	52	2659	54	2454	59
13	Al	2490	67	2666	73	2473	70	2787	61	2862	60	2788	56
19	K	1384	29	1349	27	1306	29	1172	29	1153	26	1147	26
20	Ca	7261	130	7410	119	7293	86	6998	127	7242	131	6938	189
22	Ti	168.0	2.4	176.2	3.6	167.9	2.5	176.8	2.8	178.2	2.6	176.1	3.5
23	V	652	23	672	24	649	24	656	37	649	38	606	36
24	Cr	15.30	0.35	15.75	0.31	15.22	0.32	15.34	0.41	15.57	0.38	15.20	0.42
25	Mn	108.0	3.1	107.9	3.0	105.1	3.0	105.8	6.6	105.2	6.8	98.1	6.4
26	Fe	3305	35	3385	46	3325	44	3389	51	3471	44	3433	48
27	Co	2.077	0.033	2.179	0.027	2.048	0.027	2.205	0.036	2.206	0.034	2.112	0.052
28	Ni	23.03	0.55	23.31	0.56	23.07	0.61	25.01	0.69	25.25	0.82	22.42	0.60
29	Cu	24.57	0.57	25.76	0.69	27.01	0.77	24.82	0.64	28.70	0.79	25.35	0.71
30	Zn	32.06	0.98	32.11	0.91	27.73	0.81	30.44	0.85	32.4	1.3	30.26	0.85
31	Ga	0.310	0.010	0.326	0.021	0.3284	0.0091	0.353	0.043	0.380	0.021	0.339	0.022
32	Ge	0.030	0.015	0.069	0.070	0.064	0.043	0.124	0.094	0.094	0.060	0.049	0.043
33	As	358.5	5.4	373.1	6.0	324.5	4.0	365.2	7.1	382.1	8.5	341.5	7.2
37	Rb	7.90	0.11	8.35	0.13	7.75	0.11	8.13	0.18	8.22	0.11	8.03	0.11
38	Sr	50.76	0.77	51.19	0.80	49.08	0.77	51.13	0.80	52.17	0.82	50.70	0.83
40	Zr	401	11	392	10	383	11	399	10	406	11	378	14
41	Nb	0.384	0.013	0.368	0.012	0.346	0.014	0.386	0.015	0.392	0.017	0.358	0.017
42	Mo	701	12	702	14	696	14	712	10	712	14	669	19
44	Ru	< 0.018	--	< 0.018	--	< 0.018	--	< 0.018	--	< 0.018	--	< 0.018	--
45	Rh	0.0156	0.0010	0.01601	0.00061	0.01615	0.00061	0.01089	0.00074	0.0112	0.0015	0.01120	0.00056
48	Cd	2.760	0.050	2.808	0.051	2.827	0.062	3.032	0.090	2.854	0.094	2.82	0.16
50	Sn	3.104	0.080	3.206	0.071	3.23	0.14	3.549	0.080	3.512	0.098	3.354	0.098
51	Sb	0.1150	0.0061	0.120	0.013	0.1141	0.0085	0.1144	0.0021	0.1175	0.0028	0.1086	0.0050
55	Cs	0.970	0.013	1.020	0.016	0.922	0.013	0.977	0.013	0.975	0.016	0.911	0.014

Sessions C and D CUP-2 Trace Element Data Continued[a]													
Atomic Number	**Element**	**CUP-2 C-1**	***Unc. (k=2)***	**CUP-2 C-2**	***Unc. (k=2)***	**CUP-2 C-3**	***Unc. (k=2)***	**CUP-2 D-1**	***Unc. (k=2)***	**CUP-2 D-2**	***Unc. (k=2)***	**CUP-2 D-3**	***Unc. (k=2)***
56	Ba	114.9	2.0	107.1	2.0	113.2	2.1	109.6	2.2	119.9	2.4	112.8	2.9
57	La	19.57	0.37	21.72	0.29	18.78	0.27	18.75	0.31	19.00	0.37	19.12	0.37
58	Ce	36.7	1.4	41.0	1.5	34.7	1.3	39.39	0.63	39.94	0.59	40.35	0.76
59	Pr	4.48	0.12	5.04	0.13	4.18	0.11	4.689	0.064	4.713	0.070	4.749	0.085
60	Nd	19.77	0.37	21.85	0.47	18.95	0.35	19.65	0.30	19.71	0.35	20.05	0.49
62	Sm	9.24	0.19	10.13	0.24	8.99	0.21	9.59	0.16	9.53	0.15	9.70	0.14
63	Eu	0.776	0.013	0.835	0.022	0.741	0.020	0.783	0.017	0.791	0.012	0.799	0.016
64	Gd	15.44	0.25	16.66	0.27	14.83	0.28	15.35	0.34	15.45	0.22	15.62	0.24
65	Tb	2.906	0.037	3.148	0.036	2.840	0.034	2.859	0.057	2.897	0.053	2.902	0.051
66	Dy	17.99	0.30	19.43	0.27	17.57	0.27	17.74	0.26	18.00	0.26	18.16	0.27
67	Ho	3.206	0.049	3.434	0.053	3.102	0.037	3.172	0.053	3.272	0.056	3.198	0.056
68	Er	8.46	0.11	9.04	0.13	8.044	0.099	8.42	0.18	8.45	0.14	8.54	0.13
69	Tm	1.071	0.030	1.178	0.026	1.052	0.013	1.105	0.021	1.117	0.025	1.118	0.021
70	Yb	6.54	0.11	7.15	0.11	6.318	0.093	6.72	0.24	6.68	0.13	6.73	0.12
71	Lu	0.827	0.020	0.905	0.014	0.794	0.016	0.850	0.015	0.875	0.020	0.873	0.018
72	Hf	0.2399	0.0079	0.2304	0.0063	0.244	0.013	0.250	0.017	0.287	0.023	0.300	0.037
73	Ta	0.0267	0.0022	0.0311	0.0016	0.0293	0.0019	0.0323	0.0024	0.0358	0.0020	0.0341	0.0033
74	W	12.96	0.35	13.08	0.34	12.57	0.35	12.68	0.27	12.96	0.25	12.27	0.26
75	Re	0.0280	0.0010	0.02906	0.00067	0.0268	0.0018	0.02854	0.00094	0.0297	0.0012	0.0276	0.0014
77	Ir	0.00258	0.00016	0.00269	0.00024	0.00271	0.00027	0.00278	0.00020	0.00291	0.00049	0.00274	0.00037
78	Pt	0.00329	0.00036	0.00390	0.00060	0.00397	0.00060	0.0035	0.0013	0.0046	0.0011	0.00485	0.00072
81	Tl	3.354	0.059	3.570	0.063	3.167	0.060	3.240	0.064	3.238	0.068	3.083	0.060
82	Pb	265.4	9.7	276	10	261.6	9.9	261	14	261	14	262	15
83	Bi	1.194	0.017	1.216	0.016	1.163	0.014	1.153	0.013	1.167	0.015	1.132	0.016
90	Th	1558	23	1730	25	1515	21	1503	38	1533	44	1408	40

[a] Trace element compositions for CUP-2 solutions were analyzed in triplicate during four analytical sessions in 2017: January 27 (CUP-2 A), January 30 (CUP-2 B), January 31 (CUP-2 C), and February 1 (CUP-2 D).

[b] All trace element data are reported in units of µg/g sample. Trace elements were originally measured here in units of µg/g U, and were converted to units of µg/g sample using the U content provided on the CUP-2 certificate. Note that no correction for hydration differences between trace element contents measured here on an "as received" basis and U content measured for the certificate value on a dry basis has been made.

Table 4. L_C and Average CUP-2 Trace Element Composition Compared to Certified Reference Values.

CUP-2 Trace Element Average Data					
Atomic Number	**Element**	**Lc[a]**	**CUP-2 Avg.**	***Unc. (k=2)[b]***	**Certified Value[c]**
3	Li	0.172	0.916	0.023	--
4	Be	0.33	--	--	--
5	B	3.40	51.9	1.3	51[d]
11	Na	17	4759	136	4590
12	Mg	2.2	2472	66	2290
13	Al	3.7	2599	95	--
19	K	7.5	1228	66	1100[d]
20	Ca	7.1	7094	189	6200
22	Ti	0.26	171.0	3.2	190
23	V	0.65	660	13	660[d]
24	Cr	0.13	15.36	0.32	--
25	Mn	0.37	105.8	2.1	--
26	Fe	3.2	3340	42	3110
27	Co	0.047	2.146	0.057	--
28	Ni	0.45	23.46	0.67	29
29	Cu	0.15	25.0	1.0	--
30	Zn	0.62	31.09	0.93	--
31	Ga	0.0028	0.332	0.012	--
32	Ge	0.0029	0.063	0.016	--
33	As	0.062	367	13	350
37	Rb	0.038	7.85	0.19	--
38	Sr	0.023	51.22	0.59	--
40	Zr	0.042	395.9	6.7	440[d]
41	Nb	0.0025	0.398	0.042	--
42	Mo	0.43	705.2	9.4	690
44	Ru	0.018	--	--	--
45	Rh	0.00768	0.0135	0.0016	--
48	Cd	0.152	2.884	0.070	--
50	Sn	0.016	3.33	0.10	--
51	Sb	0.0023	0.1182	0.0040	--
55	Cs	0.013	0.967	0.019	--
56	Ba	0.038	110.8	3.3	--
57	La	0.014	19.30	0.55	--
58	Ce	0.012	38.6	1.6	--
59	Pr	0.0038	4.61	0.17	--
60	Nd	0.020	19.82	0.60	--
62	Sm	0.030	9.52	0.24	--
63	Eu	0.00035	0.787	0.023	--
64	Gd	0.0021	15.53	0.43	--
65	Tb	0.00029	2.916	0.068	--
66	Dy	0.0037	18.10	0.43	--

CUP-2 Trace Element Average Data Continued					
Atomic Number	**Element**	**Lc[a]**	**CUP-2 Avg.**	***Unc. (k=2)[b]***	**Certified Value[c]**
67	Ho	0.0015	3.225	0.082	--
68	Er	0.0045	8.48	0.20	--
69	Tm	0.00044	1.109	0.030	--
70	Yb	0.0012	6.68	0.18	--
71	Lu	0.000040	0.857	0.029	--
72	Hf	0.00026	0.250	0.014	--
73	Ta	0.00035	0.0301	0.0022	--
74	W	0.15	12.97	0.26	--
75	Re	0.000072	0.02856	0.00073	--
77	Ir	0.000070	0.002758	0.000091	--
78	Pt	0.00042	0.00398	0.00041	--
81	Tl	0.0053	3.258	0.076	--
82	Pb	0.030	265.6	3.2	--
83	Bi	0.0033	1.187	0.023	--
90	Th	0.34	1550	49	--

[a] L_C = Critical level, level above which an element is detected but not necessarily quantifiable.
[b] Uncertainty on the average measured CUP-2 value is calculated as described in the text.
[c] Certified values in this table are from the CUP-2 certificate and have been converted from units of weight percent to units of µg / g sample.
[d] Indicates that the reference value is provisionally recommended.
[e] All trace element data are reported in units of µg/g sample. Trace elements were originally measured here in units of µg/g U, and were converted to units of µg/g sample using the U content provided on the CUP-2 certificate. Note that no correction for hydration differences between trace element contents measured here on an "as received" basis and U content measured for the certificate value on a dry basis has been made.

URANIUM ISOTOPE COMPOSITION

Overview

The U isotope composition of uranium-bearing materials is an important forensic signature. Natural U contains approximately 0.7% uranium-235 (^{235}U) and 99.3% uranium-238 (^{238}U). Deviations from this composition (i.e., enrichment or depletion of ^{235}U)—as well as the presence of uranium-233 (^{233}U), uranium-234 (^{234}U), and uranium-236 (^{236}U) in the material—can provide information about the provenance and nuclear processing history of the material. The U isotope composition of CUP-2 and CRM 124-2 was determined by both MC-ICP-MS and SC-ICP-MS at LANL for benchmarking purposes.

Uranium Aliquots and Chemical Purification – U Purification from Trace Contaminants

For U isotope composition analysis by both multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and single-collector inductively coupled plasma mass spectrometry (SC-ICP-MS), volumetric aliquots of the tertiary dilution of CUP-2 and associated process blank and quaternary dilution of CRM 124-2 and associated process blank were transferred into pre-cleaned Savillex PFA vials. These volumetric aliquots provided approximately 30 ng of total U for analysis. An aliquot of National Bureau of Standards (NBS) Standard Reference Material (SRM) 960 also containing approximately 30 ng of U was processed through chemistry with the samples and analyzed as a quality control material.

Sample aliquots were uncapped, dried on a hotplate at 110 ºC, and dissolved in 3 M HNO_3 for chemical purification. Uranium was purified using ion-extraction chromatography chemistry. The columns consisted of a 1 mL Eichrom UTEVA resin bed cleaned with 0.1 M HCl and conditioned with 3 M HNO_3. Samples were loaded onto the columns in 3 M HNO_3 and sample impurities were rinsed from the resin with 3 M HNO_3 washes followed by 9 M HCl and 5 M HCl washes. Uranium was then eluted from the columns into pre-cleaned Savillex PFA vials using 0.1 M HCl. The samples were dried on a hotplate at 110°C and re-dissolved in 2 mL 2% HNO_3 for mass spectrometric analysis. Sample solutions were divided for analysis by MC-ICP-MS and SC-ICP-MS as described below.

Uranium Isotope Ratio Mass Spectrometry Measurements

Multi-Collector Inductively Coupled Plasma Analysis of Samples

Following column separation, purified U sample fractions of CUP-2 and CRM 124-2 were analyzed using a Thermo Scientific Neptune Plus MC-ICP-MS outfitted with a Teledyne CETAC Aridus 3 desolvating nebulizer system (CSP 386) in two analytical sessions. Samples were introduced into the mass spectrometer as 2% HNO_3 solutions and U isotope measurements were made using a static multi-collection routine. For process blanks, ^{238}U was measured on a Faraday detector and ^{233}U, ^{234}U, ^{235}U, and ^{236}U were measured on ion counters. Samples were measured in the same configuration with the exception of ^{235}U, which was instead measured on a Faraday detector. Acid blanks were measured prior to each sample using a 2% HNO_3 solution. Faraday gain calibrations were performed immediately prior to analysis using an internally supplied voltage. All mass bias and detector gain calculations applied to the sample measurements were determined using certified reference material (CRM) U010 as a bracketing standard. A Retarding Potential Quadrupole energy filter (RPQ) reduced the contribution of low mass tailing from ^{238}U on ^{236}U. Residual mass tailing on ^{236}U and low-mass tailing from ^{238}U and ^{235}U on ^{234}U and ^{233}U were assessed by measuring ^{236}U, ^{234}U, and ^{233}U counts at four off-peak

masses (-0.50, -0.35, +0.35, +0.50 amu from peak center), fitting these counts to an exponential curve, and subtracting the calculated tail contributions from the measured signals. Certified reference material 112-A was analyzed with the samples and treated as an unknown for quality control. Additionally, SRM 960 was processed through chemistry with the samples and measured as an unknown in each analytical session, and the measured U isotope ratios for this reference material are reported in **Table 5**.

Single-Collector Inductively Coupled Plasma Analysis of Samples

Following analysis of the samples by MC-ICP-MS, the remaining purified U sample fractions were analyzed for U isotope composition using a Thermo Scientific Element XR single-collector inductively coupled plasma mass spectrometry (SC-ICP-MS; CSP 386) in two analytical sessions. Samples were introduced into the mass spectrometer as 2% HNO_3 solutions using a 400 µL/min Teflon nebulizer and a quartz dual cyclonic spray chamber. Uranium isotope measurements were made using a peak-hopping routine. For process blanks, all U isotopes were measured in pulse counting mode (< 5.0×10^6 counts per second). Samples were measured with ^{233}U, ^{234}U, ^{235}U, and ^{236}U in pulse counting mode, and ^{238}U was measured in analog mode (< 1.0×10^{10} counts per second). Pulse counting and analog detection modes were cross-calibrated prior to each analytical session using a 1 ng/g indium solution. The analog correction factor (AFC) was adjusted in the software registry until detector responses in pulse counting and analog modes were identical. Acid blanks (2% HNO_3) were measured prior to each sample in order to quantify instrument background. All mass bias calculations applied to sample measurements were determined using certified reference material (CRM) U010. Low-mass tailing on ^{236}U and ^{233}U from ^{238}U was assessed by measuring a CRM 112-A solution with a similar ^{238}U intensity to that measured in the samples at the beginning and end of each analytical session. Counts at two off-peak masses (-0.50 and +0.50 amu from peak center) were measured and fit to an exponential curve in order to calculate the tail contribution at peak center. Tailing on ^{236}U and ^{233}U relative to the measured ^{238}U intensity of each CRM 112-A analysis was averaged and these ratios were applied to each of the samples and bracketing standards in order to account for small differences in tail magnitude resulting from variable ^{238}U intensities. These calculated tail contributions were then subtracted from the measured isotope intensities. Both ^{235}U and ^{234}U were monitored for low-mass tailing from ^{238}U, but the calculated tail contribution was insignificant relative to the measured intensity (< 0.3%). Certified reference material U005A was analyzed with the sample batch and treated as an unknown for quality control. Additionally, SRM 960 was processed through chemistry with the samples and measured as an unknown in each analytical session, and the measured U isotope ratios for this reference material are reported in **Table 6**.

Uranium Isotope Ratio Uncertainty Calculations and Detection Limits

Internal uncertainties for each of the U isotope ratios reported (**Tables 5** and **6**) are combined uncertainties at the 95% confidence level (k=2), which incorporate uncertainties associated with MC-ICP-MS and SC-ICP-MS analysis, respectively.

The uncertainty reported for average U isotope ratios measured for CRM 124-2 and CUP-2 is based on three replicate determinations (measurements A, B, and C) from the same sample solution. Given the small number of replications undertaken for each sample (n=3), the 95% (2-sigma) external uncertainty provided for the average of the replicates in **Tables 5** and **6** were calculated using the following equation:

$$u = \bar{X} \pm t_{\left(1-\frac{\alpha}{2}\right),\nu}(\sigma/\sqrt{N_r})$$

Where $t_{(1-\alpha/2)}$ is the $100(1-\alpha/2)^{th}$ percentile of the t-distribution corresponding to a probability $\alpha = 0.05$ and $\nu = N_r - 1$ degrees of freedom.

The limit of detection for $^{233}U/^{238}U$, $^{234}U/^{238}U$ (for measurements via SC-ICP-MS only, which yields process blank $^{234}U/^{238}U$ below the limit of detection due to the lower instrument sensitivity compared to MC-ICP-MS), and $^{236}U/^{238}U$ ratios are calculated as three times the internal measurement uncertainty (k=1) for SRM 960 measured during each analytical session. An individual isotope ratio is reported as below the limit of detection ($< L_D$) if the measured ratio is within internal uncertainty (k=2) of the calculated limit of detection. The detection limits for each analytical session are provided in the footnotes of **Tables 5** and **6**.

Uranium Isotope Composition Results

The measured U isotope compositions obtained for CUP-2, CRM 124-2, and SRM 960 are reported in **Tables 5** and **6** below. **Table 5** provides the results obtained via MC-ICP-MS and **Table 6** provides the results measured by SC-ICP-MS.

The triplicate $^{234}U/^{238}U$ and $^{235}U/^{238}U$ measurements obtained by MC-ICP-MS for reference materials CUP-2 and CRM 124-2 agree well within uncertainty (k=2), and demonstrate that both materials have a natural U isotope composition. Neither ^{233}U nor ^{236}U were detected in CUP-2 or CRM 124-2 above the limit of detection. The results obtained for SRM 960 agree with CRM 112-A certificate values within analytical uncertainty. Reference material SRM 960 is identical to CRM 112-A: SRM 960 was re-named to CRM 112-A in 1987 (Mason et al., 2010).

The triplicate $^{234}U/^{238}U$ and $^{235}U/^{238}U$ measurements obtained by SC-ICP-MS for reference materials CUP-2 and CRM 124-2 agree at the 95% confidence level (k=2), and are consistent with the results obtained by MC-ICP-MS (**Figure 1**). However, uncertainties on the replicate measurements were comparatively better for the MC-ICP-MS measurements. The relative uncertainty on replicate $^{234}U/^{238}U$ measurements by MC-ICP-MS was 0.13% for CUP-2 and 0.10% for CRM 124-2, compared to 1.6% for CUP-2 and 1.8% for CRM 124-2 measured by SC-ICP-MS. The relative uncertainty on replicate $^{235}U/^{238}U$ measurements by MC-ICP-MS was 0.068% for CUP-2 and 0.026% for CRM 124-2, compared to 0.44% for CUP-2 and 0.43% for CRM 124-2 measured by SC-ICP-MS. Neither ^{233}U nor ^{236}U was detected by SC-ICP-MS in CUP-2 or CRM 124-2 above the limit of detection. The results obtained for SRM 960 agree with CRM 112-A certificate values within analytical uncertainty with the exception of the $^{234}U/^{238}U$ measured in SRM 960 with CUP-2; the $^{234}U/^{238}U$ value measured is biased high compared to the certificate value for that analysis.

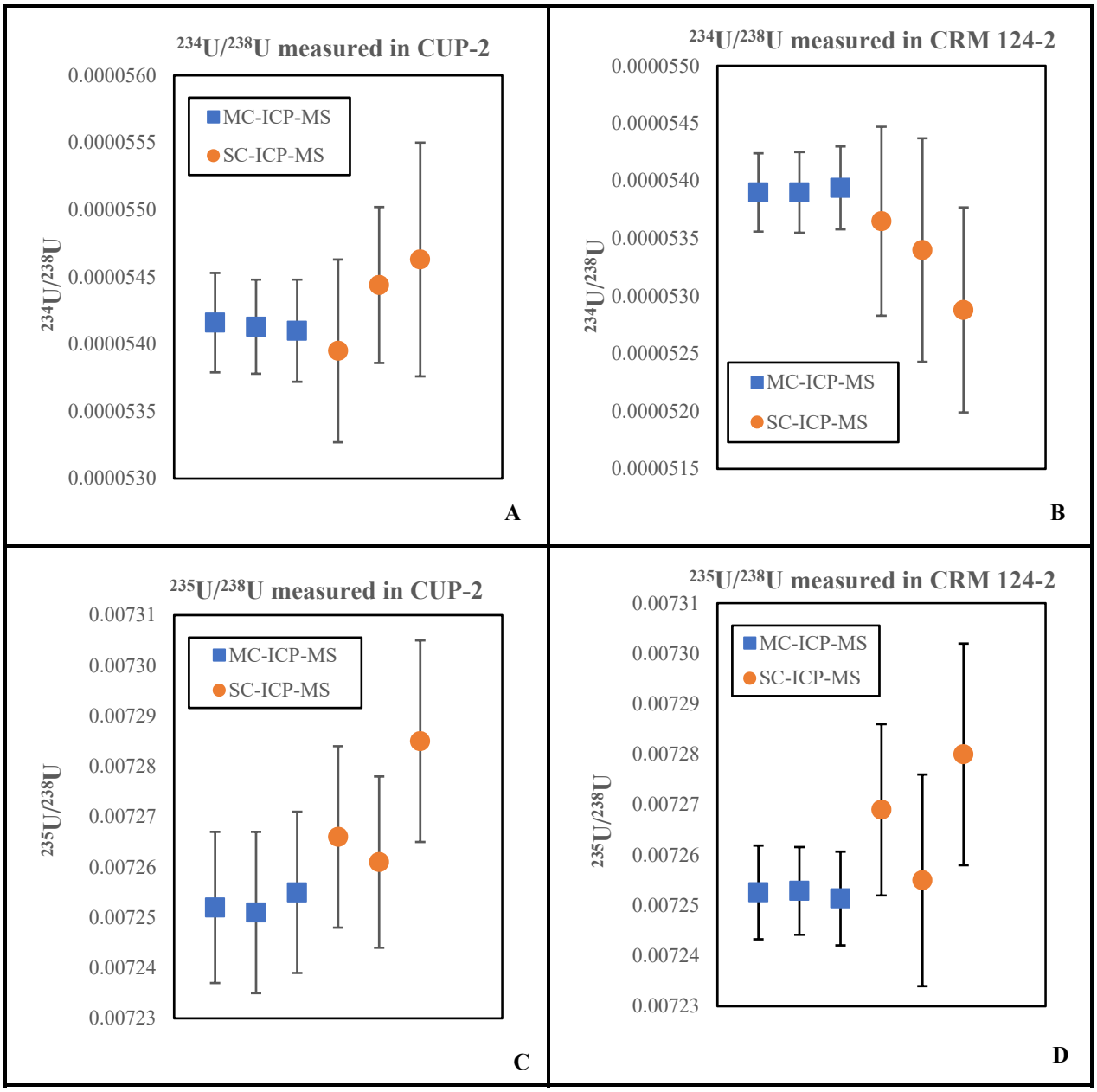

Figure 1. Measured $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios for reference materials CUP-2 and CRM 124-2. Panels A and B show measured $^{234}U/^{238}U$ ratios for CUP-2 and CRM 124-2, respectively, and panels C and D show measured $^{235}U/^{238}U$ ratios for CUP-2 and CRM 124-2. Ratios measured by MC-ICP-MS are shown in blue squares, and ratios measured by SC-ICP-MS are shown in orange circles. Error bars shown depict internal uncertainty at a coverage factor of k=2. There is good agreement between the ratios obtained by MC-ICP-MS and the ratios obtained by SC-ICP-MS.

Table 5. Measured Uranium Isotope Compositions of CUP-2 and CRM 124-2 by MC-ICP-MS

CUP-2 Data [a]								
Sample ID	**$^{233}U/^{238}U$**	**Unc. (k=2)[b]**	**$^{234}U/^{238}U$**	**Unc. (k=2)**	**$^{235}U/^{238}U$**	**Unc. (k=2)**	**$^{236}U/^{238}U$**	**Unc. (k=2)**
CUP-2 A	< L_D	< L_D	0.00005416	0.00000037	0.007252	0.000015	< L_D	< L_D
CUP-2 B	< L_D	< L_D	0.00005413	0.00000035	0.007251	0.000016	< L_D	< L_D
CUP-2 C	< L_D	< L_D	0.00005410	0.00000038	0.007255	0.000016	< L_D	< L_D
Average [c]	*< L_D*	*< L_D*	*0.000054130*	*0.000000068*	*0.0072529*	*0.0000049*	*< L_D*	*< L_D*
CRM 124-2 Data [b]								
Sample ID	**$^{233}U/^{238}U$**	**Unc. (k=2)[b]**	**$^{234}U/^{238}U$**	**Unc. (k=2)**	**$^{235}U/^{238}U$**	**Unc. (k=2)**	**$^{236}U/^{238}U$**	**Unc. (k=2)**
124-2 A	< L_D	< L_D	0.00005390	0.00000034	0.0072526	0.0000093	< L_D	< L_D
124-2 B	< L_D	< L_D	0.00005390	0.00000035	0.0072529	0.0000087	< L_D	< L_D
124-2 C	< L_D	< L_D	0.00005394	0.00000036	0.0072514	0.0000093	< L_D	< L_D
Average [c]	*< L_D*	*< L_D*	*0.000053913*	*0.000000055*	*0.0072523*	*0.0000019*	*< L_D*	*< L_D*
Process Blank Data								
Sample ID	**$^{233}U/^{238}U$**	**Unc. (k=2)[b]**	**$^{234}U/^{238}U$**	**Unc. (k=2)**	**$^{235}U/^{238}U$**	**Unc. (k=2)**	**$^{236}U/^{238}U$**	**Unc. (k=2)**
CUP-2 PB	< L_D	< L_D	0.000107	0.000022	0.0074	0.0015	< L_D	< L_D
124-2 PB	< L_D	< L_D	0.000110	0.000062	0.0088	0.0055	< L_D	< L_D
Certified Reference Material Quality Control Data								
Standard ID	**$^{233}U/^{238}U$**	**Unc. (k=2)**	**$^{234}U/^{238}U$**	**Unc. (k=2)**	**$^{235}U/^{238}U$**	**Unc. (k=2)**	**$^{236}U/^{238}U$**	**Unc. (k=2)**
SRM 960 Measured with CUP-2	< L_D	< L_D	0.00005292	0.00000036	0.007251	0.000015	< L_D	< L_D
SRM 960 Measured with CRM 124-2	< L_D	< L_D	0.00005295	0.00000039	0.0072513	0.0000087	< L_D	< L_D
SRM 960 Reference Value [f]	< 5.0×10^{-9}	--	0.000052841	0.000000082	0.0072543	0.0000040	< 5.0×10^{-9}	--

[a] Uranium isotope composition of CUP-2 analyzed on 9/23/2020.
[b] Uranium isotope composition of CRM 124-2 analyzed on 12/15/2020.
[c] Uncertainty on the averages of replicates is calculated as described in the text.
[d] Internal uncertainty based on counting statistics is reported for individual analyses at the ~95% confidence level (coverage factor k = 2).
[e] The detection limit calculated for $^{233}U/^{238}U$ was 1.5×10^{-11} during the analysis of CUP-2 and 2.0×10^{-8} during the analysis of CRM 124-2, and the detection limit for $^{236}U/^{238}U$ was 1.3×10^{-11} during the analysis of CUP-2 and 5.1×10^{-9} during the analysis of CRM 124-2.
[f] SRM 960 was re-named CRM 112-A by NBL. Certified values presented here are taken from the 2010 revision of the NBL CRM 112-A certificate.

Table 6. Measured Uranium Isotope Compositions of CUP-2 and CRM 124-2 by SC-ICP-MS

CUP-2 Data [a]								
Sample ID	**$^{233}U/^{238}U$**	**Unc. (k=2)[b]**	**$^{234}U/^{238}U$**	**Unc. (k=2)**	**$^{235}U/^{238}U$**	**Unc. (k=2)**	**$^{236}U/^{238}U$**	**Unc. (k=2)**
CUP-2 A	< L_D	< L_D	0.00005395	0.00000068	0.007266	0.000018	< L_D	< L_D
CUP-2 B	< L_D	< L_D	0.00005444	0.00000058	0.007261	0.000017	< L_D	< L_D
CUP-2 C	< L_D	< L_D	0.00005463	0.00000087	0.007285	0.000020	< L_D	< L_D
Average [c]	*< L_D*	*< L_D*	*0.00005434*	*0.00000087*	*0.007271*	*0.000032*	*< L_D*	*< L_D*
CRM 124-2 Data [b]								
Sample ID	**$^{233}U/^{238}U$**	**Unc. (k=2)[b]**	**$^{234}U/^{238}U$**	**Unc. (k=2)**	**$^{235}U/^{238}U$**	**Unc. (k=2)**	**$^{236}U/^{238}U$**	**Unc. (k=2)**
124-2 A	< L_D	< L_D	0.00005365	0.00000082	0.007269	0.000017	< L_D	< L_D
124-2 B	< L_D	< L_D	0.00005340	0.00000097	0.007255	0.000021	< L_D	< L_D
124-2 C	< L_D	< L_D	0.00005288	0.00000089	0.007280	0.000022	< L_D	< L_D
Average [c]	*< L_D*	*< L_D*	*0.00005331*	*0.00000098*	*0.007268*	*0.000031*	*< L_D*	*< L_D*
Process Blank Data								
Sample ID	**$^{233}U/^{238}U$**	**Unc. (k=2)[b]**	**$^{234}U/^{238}U$**	**Unc. (k=2)**	**$^{235}U/^{238}U$**	**Unc. (k=2)**	**$^{236}U/^{238}U$**	**Unc. (k=2)**
CUP-2 PB	< L_D	< L_D	< L_D	< L_D	0.0071	0.0011	< L_D	< L_D
124-2 PB	< L_D	< L_D	< L_D	< L_D	0.0078	0.0013	< L_D	< L_D
Certified Reference Material Quality Control Data								
Standard ID	**$^{233}U/^{238}U$**	**Unc. (k=2)**	**$^{234}U/^{238}U$**	**Unc. (k=2)**	**$^{235}U/^{238}U$**	**Unc. (k=2)**	**$^{236}U/^{238}U$**	**Unc. (k=2)**
SRM 960 Measured with CUP-2	< L_D	< L_D	0.0000540	0.0000010	0.007277	0.000020	< L_D	< L_D
SRM 960 Measured with CRM 124-2	< L_D	< L_D	0.00005316	0.00000083	0.007240	0.000017	< L_D	< L_D
SRM 960 Reference Value [f]	< 5.0×10^{-9}	--	0.000052841	0.000000082	0.0072543	0.0000040	< 5.0×10^{-9}	--

[a] Uranium isotope composition of CUP-2 analyzed on 1/21/2021.
[b] Uranium isotope composition of CRM 124-2 analyzed on 1/13/2021.
[c] Uncertainty on the averages of replicates is calculated as described in the text.
[d] Internal uncertainty based on counting statistics is reported for individual analyses at the 95% confidence level (coverage factor of k=2).
[e] The detection limit calculated for $^{233}U/^{238}U$ was 4.8×10^{-8} during the analysis of CUP-2 and 8.3×10^{-8} during the analysis of CRM 124-2, the detection limit for $^{234}U/^{238}U$ was 1.5×10^{-6} during the analysis of CUP-2 and 1.2×10^{-6} during the analysis of CRM 124-2, and the detection limit for $^{236}U/^{238}U$ was 6.2×10^{-8} during the analysis of CUP-2 and 1.0×10^{-7} during the analysis of CRM 124-2.
[f] SRM 960 was re-named CRM 112-A by NBL. Certified values presented here are taken from the 2010 revision of the NBL CRM 112-A certificate.

SUMMARY

This report details the LANL contributions in support of an interlaboratory benchmarking collaboration between LANL, LLNL, and Necsa. As part of this collaboration, LANL analyzed trace element abundances and the U isotope composition of reference materials CUP-2 and CRM 124-2. The analytical methods and results described in this report are meant for comparison to the methods employed and results obtained by LLNL and Necsa.

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